Proceedings for the Joint U.S. Russia Conference on Advances in Materials Science
SAND2009-3883C

Self-diffusion in Mo using the AM05 density functional

T.R. Mattsson[*1], N. Sandberg[†], R. Armiento[‡], A.E. Mattsson[*]

*Sandia National Laboratories, Albuquerque, NM 87185, USA.
† Royal Institute of Technology, Stockholm, SE-100 44, SWEDEN.
‡ University of Beyreuth, Beyreuth, D-95440, GERMANY.

Vacancy diffusion is the most important microscopic mechanism for mass-transport in solids. While vacancy diffusion in fcc metals is relatively well understood from a microscopic perspective, the same does not hold true for bcc metals. We present first-principles simulations using the AM05 density functional of vacancy diffusion in Mo. The calculated self-diffusion coefficient is in quantitative agreement with available experimental data. We also discuss the excellent performance of AM05 for lattice constants and bulk moduli.

Introduction

Solids are never perfect, and the importance of defects like vacancies, interstitials, and dislocations to the properties of materials can hardly be overstated. Mass transport in solids is dominated by vacancy motion, radiation creates vacancies that can nucleate and grow voids, and the motion of dislocations is important for material strenght. There are thus ample reasons to from a microscopic perspective understand, and ultimately be able to predict, properties of defects in solids, for example vacancies.

Early work applying density functional theory [1] (DFT) to study transition metal vacancies [2] used the LDA exchange correlation functional, was computationally restricted to relatively small unit cells, and structural relaxation was beyond reach. In retrospect somewhat surprisingly, these pioneering calculations came out in very good agreement with experimental data for the vacancy formation energy. However, it turned out to be difficult to improve upon them. For example, when using larger super cells and including structural relaxation, the calculated vacancy formation energies were lowered, away from experimental data. In addition, although generalized gradient exchange-correlation functionals like Perdew-Wang-91 (PW91) [3] and Perdew Burke, Ernzerhof (PBE) [4] improve upon LDA for lattice constants and cohesive energies, they lower vacancy formation energies even further, worsening the DFT calculations.

We solved this paradox in references [5] and [6] by post-processing the DFT calculations. The confusion regarding DFT calculations of vacancy formation energies was due to different intrinsic surface error of LDA and PW91. By correcting for it [6], we were able to reconcile the different results and quantify the contributions from structural relaxation, large super cells, and exchange-correlation functional [6]. The post-processing correction method, however, has limitations and most importantly, it cannot be used to correct molecular dynamics (MD) calculations. For MD to work in the context of

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[1] trmatts@sandia.gov

vacancies, the surface intrinsic error correction has to be incorporated into the exchange-correlation (xc) functional itself [7].

In this paper, we have studied vacancy formation and diffusion in Mo as an example of a bcc metal with strongly non-Arrhenius behavior for self-diffusion. We find that DFT based MD simulations reach quantitative agreement with available experimental data on the self-diffusion coefficient.

Method

Density Functional Theory

Density functional theory [1] is a formally exact reformulation of the Schrödinger equation. In DFT, the fundamental property is the density of electrons in three-dimensional real space, ρ(x,y,z), *regardless of how many electrons are in the system*. In contrast, for N electrons, the Schrödinger equation is 3N dimensional. For systems with many electrons, DFT is decidedly faster. The key term in the Kohn-Sham equations is the approximation of the many-body interaction, the so-called exchange-correlation functional. The first approximation, the local density approximation (LDA) was put forward already in the pioneering work [1]. LDA works excellently for many systems, in particular metals, but rather poorly for molecules. Functionals taking the gradient of the density in to account were developed later by many: Becke, Lee, Yang, and Parr (BLYP) [8], PW91 [3], PBE [4], and revised PBE (RPBE) [9]. Gradient corrected functionals improved significantly upon LDA for molecular systems. However, only PW91 and PBE are widely used for solid-state problems. At the time, PW91 and PBE were considered equivalent, and are often referred as the generalized gradient approximation (GGA). Only recently was it discovered that PW91 and PBE can, and do, yield different results [10].

As computers became faster and codes more efficient, it became possible to apply DFT also to solid-state problems that require several tens of atoms in the super-cell: surfaces, defects, interfaces, and alloys. As this development accelerated, there were only two xc-functionals available: LDA or GGA (PW91/PBE). This changed in 2005.

The AM05 functional

Development of an exchange-correlation functional based on a surface model system was discussed by Kohn and Mattsson [11]. The approach was later formalized and generalized in the subsystem functional scheme [12] and implemented in the AM05 functional [7]. AM05 involves two model systems: the uniform electron gas is used in regions that are locally bulk-like and a surface functional (derived from the Airy gas [11] and jellium surfaces) for regions that are locally surface-like. By including two different exact reference systems, AM05 constitutes a systematic improvement over LDA. In the first paper, it was demonstrated that AM05 gives lattice constants and bulk moduli to high accuracy for Al (simple metal), Pt (transition metal) and Si (semi conductor) [7]. More recently, by comparing results for 20 solids (Al, Ag, Pd, Rh, Cu, GaAs, GaP, Na, NaF, NaCl, MgO, SiC, Si, C, GaN, BN, BP, Li, LiF, and LiCl), it was confirmed that AM05 yields lattice constants that on average are significantly better than LDA, PBE, RPBE, and BLYP [13], mean absolute errors are shown in Figure 1. The functional employed in this work, AM05, performs on average as well as computationally significantly more expensive hybrids.

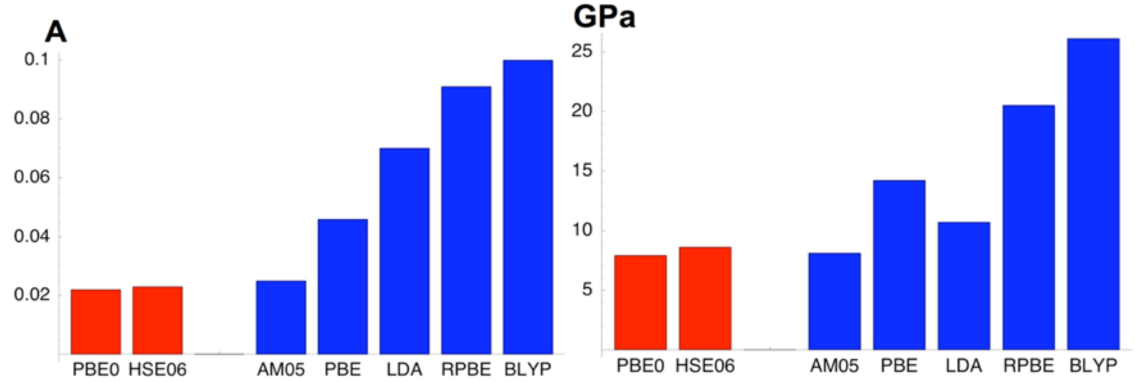

Figure 1. Mean absolute errors for lattice constant and bulk modulus for 20 solids with seven functionals: PBE0 and HSE06 [14] and AM05, PBE, LDA, RPBE, and BLYP [13].

Code and computational details

The MD simulations were performed with a massively parallel version of the projector augmented wave [15] (PAW) core-potential code VASP 5.1.40 [16] on CRAY-XT [17] using stringent convergence settings [18]. The PAW implementation in VASP 5.1 allows use of multiple XC functionals on the same set of core potentials while retaining high precision [13]. We used the 6 valence electron Mo PAW PBE core function of 08Apr2002. While it has a nominal plane-wave cutoff (ENMAX) of 224.584 eV, we used 400 eV to converge the pressure to a few percent. The electronic structure is minimized to 10^{-5} eV convergence criterium. Real-space projections were not applied. Convergence with respect to kpoints was investigated by comparing energies for gamma point (0,0,0), mean-value point (1/4,1/4,1/4), and Monkhorst-Pack grids with and 2^3 and 4^3 sampling. The mean-value point has proven to yield results that are significantly improved compared to gamma-only calculations.

The DFT-MD simulations are the most computationally demanding parts of the present work, but are necessary for the study of the an-harmonic contributions to the formation and migration energies. We use velocity Verlet time-integration with a time-step of 2.0 fs resulting in about five electronic iterations being required per ionic step at 2800 K. The simulations are kept in the NVT ensemble with a Nose thermostat (80 fs time-constant). The electronic states are distributed according to the finite-temperature formulation of DFT [19], the use of which is very important for obtaining accurate thermodynamic properties [20]. Structural optimization was used to find the low-temperature limit of the vacancy formation energy and the migration activation energy in 128 atom super-cells. The corresponding prefactors for vacancy formation and migration where obtained by calculating the force-constant matrix via finite displacements [21], this was done in 54 atom unit cells. Static calculations for LDA and PBE were done with VASP 4.6. All AM05 calculations were done using VASP 5.1.40.

Vacancy formation enthalpy and vacancy hopping from MD

The vacancy formation energy was obtained by comparing thermally averaged energies in a system containing a vacancy, with that in a bulk system, using DFT-MD. In order to unambiguously locate the vacancy at each time step, we use a model potential [22] to quench a copy of each atomic configuration, and associate the empty lattice site with the position of the vacancy [23] hereby obtaining a trajectory in time of the vacancy migration. By comparing long model potential simulations in 127, 1023 and 3455 atom systems, we conclude that the jump-rate in a 127-atom system is representative of that in larger systems to within 5%.

Results

Vacancy formation enthalpy

The result for vacancy formation enthalpy calculated from long DFT-MD simulations is shown in Figure 2. The strong temperature dependence is well described by a quadratic form [24]. Figure 2 also demonstrates the importance of including finite electronic temperature.

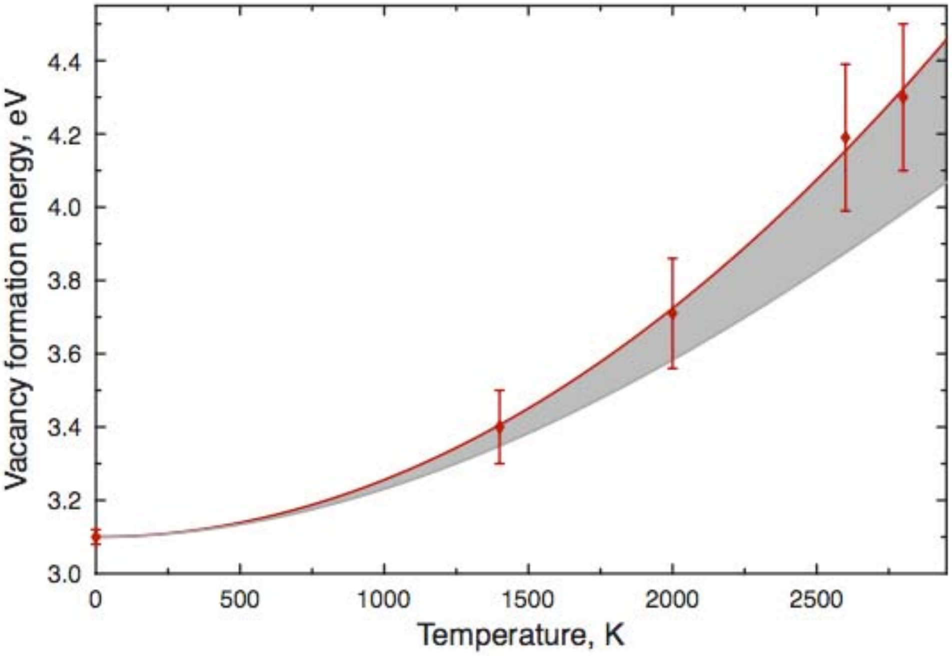

Figure 2. Mo vacancy formation energy as function of temperature [24]. The shaded contribution is from the electronic entropy and error bars are 2σ statistical uncertainty calculated by block-averaging.

Self diffusion

Based on the hopping rates obtained in the MD simulations, we estimate the vacancy diffusion coefficient. Since the formation energy is known as a function of temperature (Figure 2), we use it to find the migration energy as a function of temperature to match self-diffusion from room temperature to melting. The calculated self-diffusion is shown in Figure 3. The AM05 results are in quantitative agreement with experimental data when considering the difficulties involved in accurate calculations of point defects and point-defect kinetics in transition metals [6]. There is a significant difference between using PBE and AM05, confirming the central importance of the exchange-correlation functional also for solid-state systems.

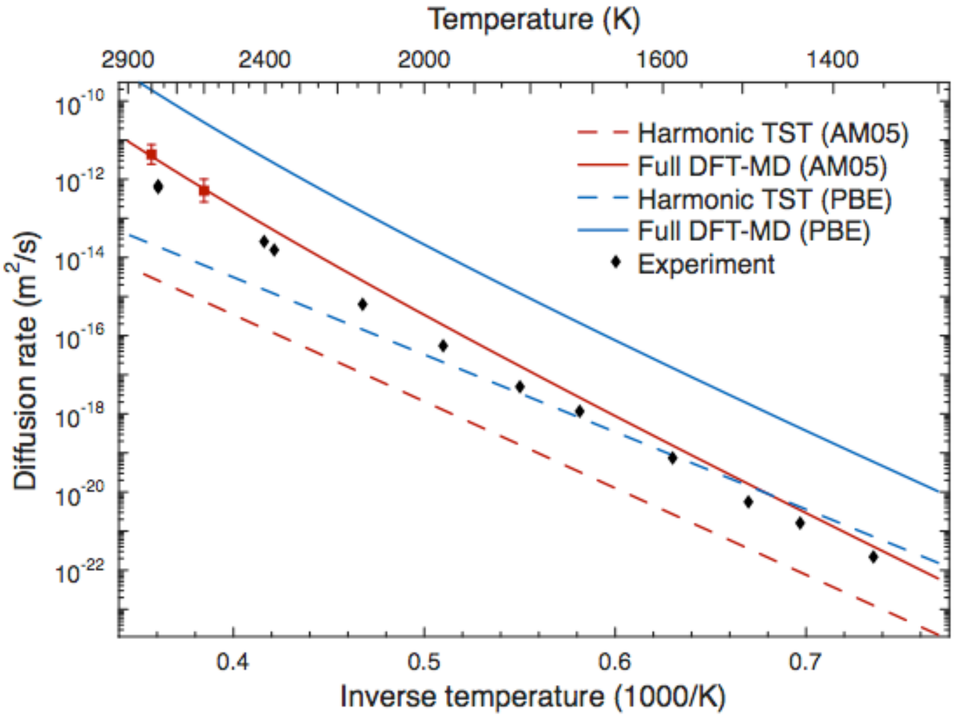

Figure 2. Calculated Mo self-diffusion rate as a function of temperature [24]; with experimental data by Maier, Mehrer, and Rein [25]. Red squares are from the long direct MD simulations of hopping, the red line is from vacancy formation energy in Fig 2 combined with a vacancy migration energy to fit the MD diffusion.

Conclusions

We have shown that a quantitative microscopic model of vacancy diffusion in bcc metals can be founded on DFT simulations given that the xc-functional is of high fidelity and MD simulations are performed close to the melting point. Given the large change in vacancy formation energy as a function of temperature as well as the importance of including finite temperature treatment of the electronic states, we infer that the use of a classical model potential over the entire interval in temperature is an approach that faces formidable challenges to correctly describe defects in Mo, and likely other bcc metals.

Acknowledgements

We thank Göran Grimvall for discussions and Odd Runevall for performing some of the verification calculations. We also thank Georg Kresse for the early opportunity to employ VASP 5.1 and Paul Kent for sharing Cray XT4 code modifications. The MD calculations were run on Red Storm at Sandia High Performance Computing and we thank Dennis Dinge for technical support on the machine. R.A. gratefully acknowledges support from the Alexander von Humboldt Foundation.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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